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Aerosols in Northern Morocco: Input pathways and their chemical fingerprint

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ABSTRACT

The Mediterranean basin is one of the most sensitive regions in the world regarding climate change and air quality. Deserts and marine aerosols combine with combustion aerosols from maritime traffic, large urban centers, and at a larger scale from populated industrialized regions in Europe. From Tetouan city located in the North of Morocco, we attempted to better figure out the main aerosol transport pathways and their respective aerosol load and chemical profile by examining air mass back trajectory patterns and aerosol chemical compositions from May 2011 to April 2012. The back trajectory analysis throughout the sampling period led to four clusters, for which meteorological conditions and aerosol chemical characteristics have been investigated. The most frequent cluster (CL3: 39%) corresponds to polluted air masses coming from the Mediterranean Basin, characterized by urban and marine vessels emissions out of Spain and of Northern Africa. Two other polluted clusters were characterized. One is of local origin (CL1: 22%), with a marked contribution from urban aerosols (Rabat, Casablanca) and from biomass burning aerosols. The second (CL2: 32%) defines air masses from the near Atlantic Ocean, affected by pollutants emitted from the Iberian coast. A fourth cluster (CL4: 7%) is characterized by rather clean, fast and rainy oceanic air masses, influenced during their last 24 h before reaching Tetouan by similar sources with those affecting CL2, but to a lesser extent.

The chemical data show that carbonaceous species are found in the fine aerosols fraction and are generally from local primary sources (low OC/EC) rather than long-range transported. In addition to fresh traffic and maritime vessel aerosols, our results suggest the contribution of local biomass burning.

1. Introduction

The Mediterranean basin has been described as one of the most sensitive regions of the world regarding climate and air quality (Doche et al., 2014). In the last two decades, international research projects have addressed specific questions about air pollution and transport mechanisms over the basin (e.g. MECAPIP, PYREX, PAUR I and II, MEDUSE, ESCOMPTE, MINOS). In the past five years until now, aerosols have been more particularly studied for their radiative properties (Sicard et al., 2016; Mallet et al., 2016). Ground-based stations are located in the northern part of the basin, but no observations are considered from the Northern African coast.

In Morocco, aerosols or particulate matter (PM) have been investigated for their relation with meteorological parameters (Tahri et al., 2013), their chemical composition (Zghaid et al., 2009; Bounakhla et al., 2009), and their sources (Ait Bouh et al., 2014). The impacts of aerosols on health have been studied using mortality data, occurrence data of asthma attacks (Mohammedia Airpol, 2003) and of respiratory symptoms among asthmatic children (Casa Airpol, 2000). But, to our knowledge, the determination of the respective inputs of local, regional and long-range pollution sources to the aerosol mix in Morocco has never been conducted.

Several methods are commonly used to define the possible sources of atmospheric aerosol that contribute to a receptor site. Statistical methods, like positive matrix factorization and factor analysis, are powerful methods to determine source profiles based on large number of chemical species. However, they generally cannot provide useful information about the locations of the possible sources, or the effects of regions downwind of receptor sites (Karaca and Camci, 2010). Alternatively, the use of methods based on back trajectories provide detailed

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information about the source regions, the air mass pathways at the local, regional and even long-range scales. Many studies demonstrated how important is the information on air mass back trajectories in the assessment of transport pathways of air pollutants, especially the long-range transport (Abdalmogith and Harrison, 2005; Wang et al., 2010).

The present work aims at characterizing the origins of aerosols and their concentration levels over the western end of the basin. A continuous aerosol measurement was carried out during a one-year period in Tetouan city, which is one of the two major Moroccan cities on the Mediterranean Sea, located 40 km away from Tangiers and the Gibraltar Straight. Air quality in Tetouan urban area is mainly affected by aerosols which originate from European and African urban areas, forest fires, and fossil fuel burning emitted by commercial ships (Diapouli et al., 2017; Barnaba and Gobbi, 2004). Lyamani et al. (2015) reported that high aerosol loads over Alborán were mainly associated with desert dust transport from arid areas in North Africa. Our study describes the major air mass pathways that reach Tetouan city in terms of meteorology and aerosol chemical composition, in an attempt to point out the main sources of aerosols affecting Northern Morocco air quality.

2. Measurement and techniques

2.1. Aerosol sampling

Aerosol sampling was performed from May 2011 to April 2012 on the campus of the Museum of Art, located about 1.5 km west of the historical city center (Médina), in an urban residential area. The instruments and sampling lines were set up on a terraced roof, approximately 15 m above ground level (35.57°N, 5.36°W). PM_{10} and $PM_{2.5}$ (aerosols < 10 μm and < 2.5 μm in diameter) were collected on 47-mm diameter Teflon filters (*Pall*®) for the gravimetric and soluble inorganic ion analyses, and on 47-mm diameter Quartz fiber filters (*Whatman*®) for the determination of the aerosol carbon content. The PM sampling duration was adapted in order to maintain the cutoff and the analysis reliability. Sampling frequency was typically 20 min every hour for a week and could be reduced during strong dust periods. Each week, two sampling periods were considered: weekdays and weekends. The filter holders were manipulated in a clean room, and the filters were handled with gloved hands and Teflon tweezers. The filtration system comprises five units: the PM cut-off cyclone manufactured by URG® (model 2000-30ENB) operating at 1 m^3/h, a flow regulator, a filter-holder, a pump and a volume counter. All units were connected by semi-rigid tubing.

2.2. Gravimetric measurements

The filters from filtration system were weighed before and after sampling, using a Mettler Microbalance UMT3 with 1 μg sensitivity. Filter weighing was achieved after 24-h equilibrium at room temperature with atmospheric relative humidity (RH) maintained below 30%. The uncertainty for each weighing was typically of the order of 20 μg, which represents an average uncertainty of 2.0% and 3.8% for PM measurements in the fine and the coarse fractions, respectively. Each filter was passed through a Haug U-electrode ionizer just before weighing to reduce the effects of static charge. Loaded filters were treated identically before being weighed for the gravimetric determination of PM mass.

2.3. Carbonaceous aerosols

Carbonaceous aerosols include elemental carbon (EC), organic carbon (OC) and inorganic carbon (carbonates). Carbon determination was performed using the two-step combustion approach developed by Cachier et al. (1989). This method was developed to minimize the two major artifacts affecting thermal procedures: (i) the adsorption of volatile organic compounds on the filter (positive artefact), and (ii) the evaporation of semi-volatile organic matter (negative artefact). In brief, the samples deposited onto the quartz filters were first exposed to HCl vapor during 24-hrs to remove carbonates. Step 1 consisted in a pre-combustion at 340 °C under O_2 for 2 h in order to remove the OC component. Step 2 consisted in the oxidation of the remaining EC at 1200 °C under O_2. The resulting CO_2 was eventually titrated by coulometry (Ströhlein Coulomat 702C). The other part of the filter underwent step 2 only, so that the content of TC was determined. The difference (TC - EC) yielded OC concentration. In our results, EC and OC were detected on field blanks and averaged 0.18 and 0.76 μgC/m3. Blank corrections were then performed and respectively represent on average 2% and 7% of the EC and OC measurements performed during the campaign. Following the conclusions of Cachier et al. (1989), uncertainty in the EC and OC measurements is estimated to be on the order of 5%. Typically for our dataset, this uncertainty corresponds to 4.5% and 7.6%, on average, for our EC and OC mass concentrations; it is comparable to the uncertainty in the gravimetric PM measurements. A conversion factor in the range 1.2–1.4 ± 30% was applied to OC to estimate the amount of particulate organic matter (POM). The conversion factor and its uncertainty was determined following the method described in Guinot et al. (2007).

2.4. Water soluble inorganic aerosols

Ion analysis was performed on the Teflon filters collected for PM_{10} and $PM_{2.5}$. Half of each sample filter was put inside a vial together with 15 mL of MilliQ water that had a resistivity typically less than 18Ω. Aerosol extraction from the filter matrix to the solution was performed by putting the vials in an ultrasonic bath for 45 min. The analysis of the major soluble inorganic cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) was performed using on a 4-mm diameter CS12 column associated to an ion chromatograph (IC) (Dionex, model DX-600) equipped with a reagent free system (automated eluent generation and self-regenerating suppression). The analysis of the major inorganic anions (SO_4^{2-}, NO_3^-, Cl^-, NO_2^-, $HCOO^-$, CH_3COO^-, $C_2O_4^{2-}$) was performed using a 4-mm diameter AS11 column associated to an IC (Dionex, model DX-600) equipped with a reagent free system. Blank filters were systematically taken in the field and treated the same way, and did not show any significant contamination during sampling, handling or shipping. Based on a maximum uncertainty of 10 ppb in the analysis of the major inorganic ions, we estimated a maximum uncertainty of 0.05 μg/m3 (less than 1%) for each ion concentration presented in Table 2.

2.5. Meteorological data

Meteorological data records were obtained from the weather station Sania-Ramel (35.58°N, 5.33°W) located in Tetouan, about 3.3 km from our study site (http://www.tutiempo.net). The meteorological data include wind speed, relative humidity, precipitations and air temperature.

2.6. Air mass trajectories

Air mass back trajectories have been frequently used to assess long-range transport patterns of air pollutants. Our study used the Hybrid Single-Particle Lagrangian Integrated Trajectory model, HYSPLIT™ (Version 4.7), developed by the Air Resources Laboratory (ARL) of the National Oceanic and Atmospheric Administration (NOAA) (Draxler and Rolph, 2003; Draxler et al., 2005) to compute simple trajectories from complex dispersion and deposition simulations, using particle approaches within a Lagrangian framework. The meteorological data gridded at regular time intervals and required to run the model were obtained from routine archives. The data used for trajectory calculations were provided by the Global Data Assimilation System (GDAS) current 7 days archive. The global data files are on their native latitude-longitude grid and are archived as one file per week. The basic output of

the HYSPLIT model is hourly trajectory endpoints indicating the geographical location and the height of the air parcel. We hence generated 48-h back trajectory data for the years 2010–2013 (one trajectory per day) at 12 UTC (Coordinated Universal Time). The error associated with HYSPLIT air mass trajectory generation is estimated to be anywhere from 15% to 30% and depends on the distance the trajectory crossed (Draxler, 1991).

The choice of arriving altitudes for the back trajectory calculation is an important step. The average mixing layer height, determined by HYSPLIT for the years 2011 and 2012 was 450 m and ranged from 9 m to 2235 m. This height of 500 m was thus considered to be within the mean annual mixed-layer height over Tetouan. The arriving altitude of 1000 m was also chosen for back trajectory calculation in order to check for significant differences in clustering results.

In order to group the back trajectories into distinct transport patterns, trajectory cluster analysis has been used. This analysis method has been suggested by Moody and Galloway (1998) to group 3-day trajectories at two pressure levels to evaluate long-range contributions to precipitation samples collected in Bermuda. The cluster analysis method was also applied by Dorling et al. (1992) to distinguish distinct flow patterns in South Scotland. Karaca and Camci (2010) used self-organizing maps (SOM) to cluster groups of similar air masses for PM_{10} episodic events and to evaluate the effects of long-range transport patterns of air masses to the regional PM profile in Istanbul. Finally, cluster analysis method has been used to obtain groups of synoptic back trajectories for each sampling day to evaluate potential pollution sources (Tsakovski et al., 2009).

Air mass back trajectory data were therefore assigned to clusters according to their speed, direction, origins, altitudes, transport patterns and meteorological conditions using the clustering algorithm within HYSPLIT-4. Clustering starts by assigning each trajectory to its own cluster, so that there are i clusters with $j=1$ trajectories in each cluster. In each iteration, the cluster number is reduced by one as two clusters are merged together. So that after the 2nd iteration there will be *i-1* clusters consisting of one cluster with two trajectories, and the remainder with one trajectory. This process continues until only one cluster remains. Further description of clustering process can be found in HYSPLIT-4 User's Guide-Version 4 published by NOAA's ARL.

A total of 1487 back trajectories at both altitudes were computed and used in the cluster analysis. The results showed that the pathway of the air mass back trajectories obtained for both altitudes, 500 m and 1000 m, were in agreement for most of the days in the period 2010–2013. Therefore, trajectories with arriving altitudes within the range 500–1000 m could be considered to be associated to the same air mass. Further results in this article consider an arriving altitude of 500 m. A similar approach was followed by Karaca and Camci (2010) in Istanbul.

3. Results and discussion

3.1. Tetouan climatology

Fig. 1 presents the monthly variations of temperature, rainfall, RH and wind speed between 2010 and 2013, which includes our period of study from May 2011 to April 2012. Winters and summers have contrasted characteristics, while springs and autumns can be considered as inter seasons, with transitional weather conditions. The highest temperatures occur in summer, with monthly means ranging 25–27 °C, against 11–15 °C in January and February. Relative humidity (RH) stands between 50% in summer, up to 75% in autumn and winter under the influence of air masses from the Atlantic Ocean and the Mediterranean Sea. Similarly, Tetouan receives most of its rainfall in winter and autumn, while minima are recorded in June and July. Rainfall intensity can have a strong year-to-year variability. Tetouan is generally windy in winters and springs, wind speed averaging 18 km/h, while diurnal breeze conditions characterize the summer months.

3.2. Air mass back trajectories clustering

Figs. 2 and 3 present the 8 clusters of transport patterns and elevation computed from 1487 back trajectories arriving at Tetouan from January 2010 to December 2013. Five major transport patterns can be observed: Oceanic (37% of the time, clusters (or CL) 1, 2, 4), local (26%, CL6), Mediterranean (24%, CL7, 8), West coast of Morocco (7%, CL3), and Europe (6%, CL5). The air masses from Europe travel above 800 m in altitude until they approach Morocco. On the contrary, the air masses from the Western coast of Morocco (CL3) and of local origin (CL6) remain below 800 m for the 48 h before reaching Tetouan. The other clusters display comparable transport elevation profiles, i.e., air masses are located above 800 m the day before reaching Tetouan, between 500 and 800 m for the last 24 h.

3.3. Year-to-year variability of clustered air mass back trajectories

This interannual variability of the final mean back trajectories resulting from the clustering process was examined for the years 2010, 2011, 2012 and 2013. For each year, the relative occurrence of the different clusters is presented in Fig. 4. Overall, air masses coming from the Northern and Western sectors generally accounted for 2/3 of the year, local recirculation for 1/3. Particularities raised in 2010, the only year accounting for slow southerly winds, and in 2011 and 2013, as strong winds from the north then occurred over very short periods of time. As for the period of experiment (May 2011–April 2012), the cluster pattern appears comparable to the mean pattern obtained for the period 2010–2013.

3.4. Field experiment back trajectory clusters

366 back trajectories computed for the period May 2011–April 2012 were categorized into four clusters, for which geographical and elevation patterns are depicted in Fig. 5, and additional characteristics are provided in Table 1. Clusters with less than 5 trajectories were not taken into consideration.

The study period is dominated (39% of the time) by CL3 when air masses travel at moderate speed (4.4 m/s on average) over the Mediterranean Sea, and especially at low altitudes (below 500 m) along the coasts of Spain and Northern Africa over the last 18 h before reaching Tetouan. CL2 (32%) corresponds to air masses coming from the Atlantic Ocean at moderate speed (4.7 m/s on average) and rather low altitude (670 m on average), across Portugal and later Northern Morocco. CL2 air masses travel well below 500 m for the last 18 h while passing over the mouth of the Strait of Gibraltar. CL4 (7%) follows a similar path, but at much higher speed (6.8 m/s) and, despite its limited occurrence, brought almost half (44%) of the rainfall collected during the experiment, in the form of showers. Finally, CL1 (22%) defines air masses moving slowly (3.1 m/s) at similar altitudes (610 ± 100 m on average) over the local continental and coastal environments with no defined path.

3.5. PM concentration associated to clusters

Tables 1 and 2 provide meteorological and aerosol chemical characteristics observed in Tetouan for each of the four clusters. Mineral dust content was estimated from nss-Ca^{2+} using the method detailed in Guinot et al. (2007), and a conversion factor and its uncertainty of 0.12 ± 40% x dust = nss-Ca^{2+} was determined. Sea salt concentrations were estimated as:

[Sea salt] = [Na^+] + [Cl^-] + [Mg^{2+}] + [ss-K^+] + [ss-Ca^{2+}] + [ss-SO_4^{2-}] (Sciare et al., 2005).

Based on seawater composition, sea salt sulfate [ss-SO_4^{2-}] = 0.252 x [Na^+]; [ss-K^+] = 0.036 x [Na^+]; [ss-Ca^{2+}] = 0.038 x [Na^+].

CL4, which is defined by fast air masses from the Atlantic Ocean ("Ocean Fast"), is distinguished from the other clusters by low pressures

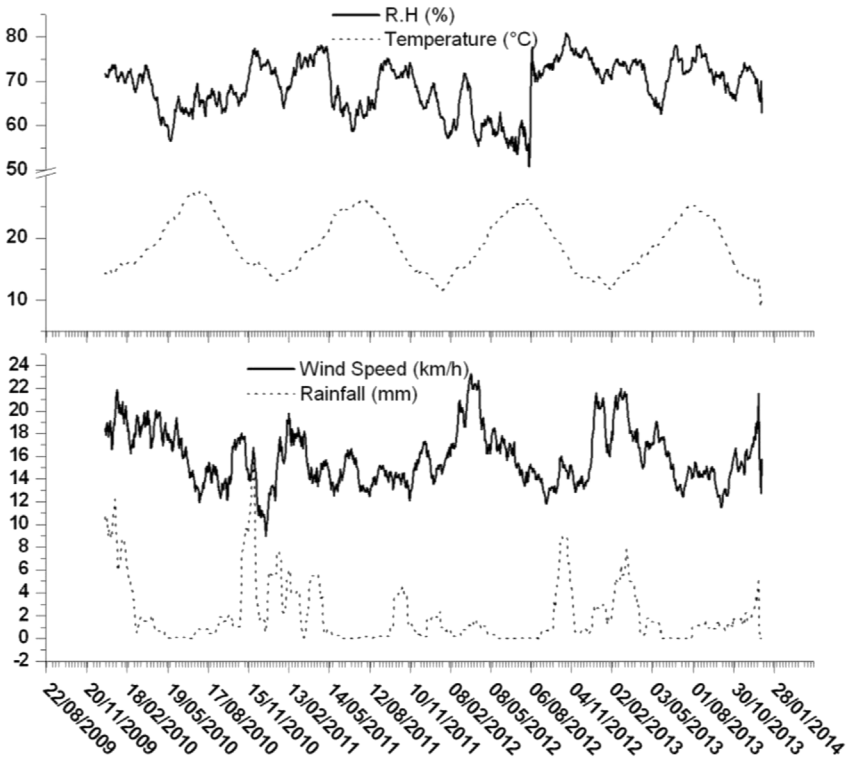

Fig. 1. Records of temperature (°C), rainfall (mm), wind speed (km/h) and relative humidity (%) derived from daily measurements at Tetouan city in 2010–2013 (30-day simple moving average).

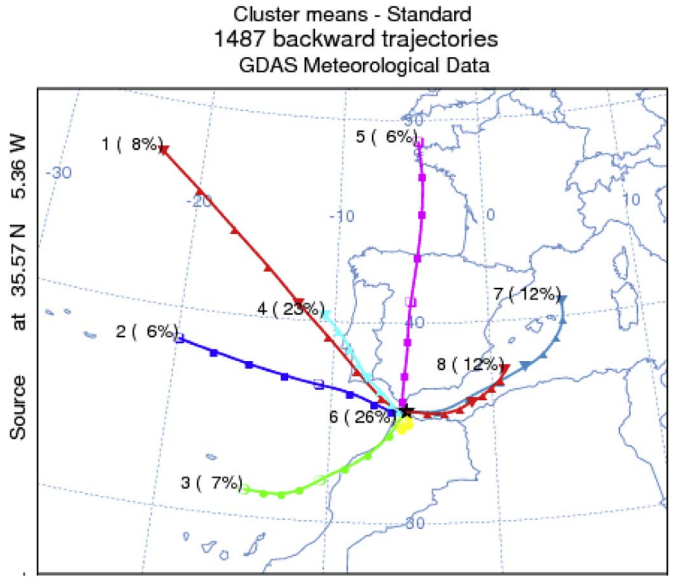

Fig. 2. Mean trajectories arriving at Tetouan from January 2010 to December 2013 classified into 8 trajectory clusters.

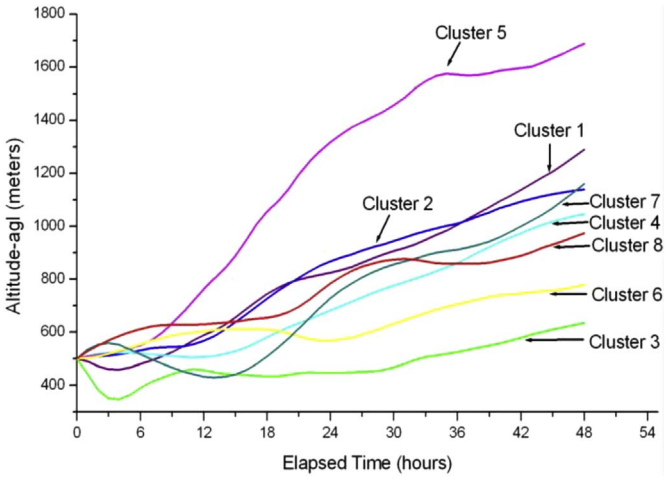

Fig. 3. Mean altitudes of each back trajectory cluster.

(relatively high boundary layer height), moderate RH but heavy rainfall episodes, and consequently leads to the lowest aerosol mass concentrations in Tetouan. In the coarse aerosol mass, sea salts dominate, as expected. Furthermore, the mass fraction of nitrate is higher in coarse fraction which is indeed corresponding to aged sea salt. But in the fine aerosol fraction, EC and POM levels together contribute to 2/3 of the fine aerosol mass, a figure comparable to the three other clusters, indicating aerosol of anthropogenic origins.

The other oceanic cluster, CL2, is also defined as “Ocean Slow” in the Tables. The 48-h pathway of CL2 corresponds to the one followed in its second half (last 24 h) by CL4, but their characteristics are rather different: CL2 is associated to about 25% higher fine aerosol mass levels, mild temperatures, while the total amount of rainfall in CL2 is more than five times lower than in CL4. In the fine mode, CL2 like CL4 is characterized by relatively high concentrations of carbonaceous aerosols. But CL2 is distinguished by significant concentrations of fine sulfate ammonium, whereas semi-volatile acids (SO2, HNO3, and organics) do not seem to be captured onto the coarse particles, despite significant amounts of mineral (basic) dust.

CL1 defines local air masses, slowly traveling from the oceanic coast over the populated areas of Casablanca and Rabat towards Tetouan. Fine and coarse aerosol mass concentrations are comparable to those of CL2 (Ocean Slow). The rather low OC/EC ratio (1.93) suggests that carbonaceous aerosols related to CL1 are rather locally emitted by traffic than long-range transported, and mainly concentrated in the fine mode. Indeed, POM and EC are minor constituents of the coarse fraction, while they predominate in the fine fraction.

CL3 corresponds to air masses coming from the Mediterranean Basin. CL3 is the most frequent cluster, the most humid (> 70%), and the most polluted by fine aerosols of the four clusters. Indeed, over the

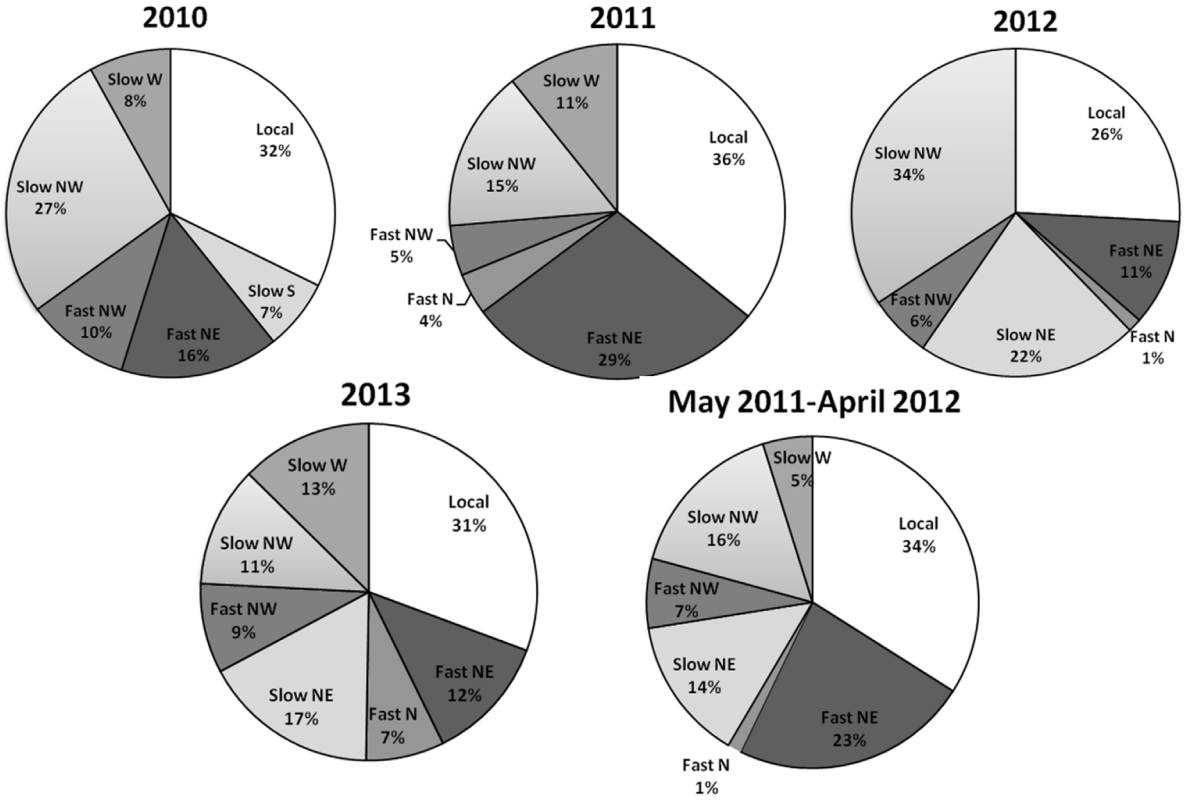

Fig. 4. Occurrence rates of each cluster for the years 2010, 2011, 2012 and 2013 and over the field experiment period from May 2011 to April 2012.

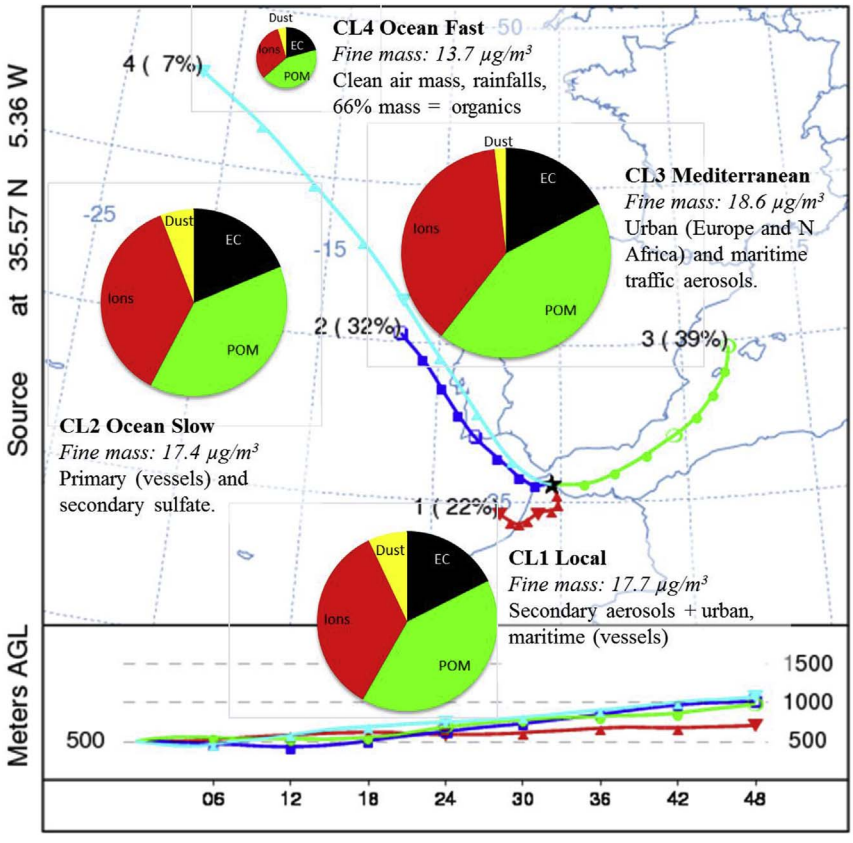

Fig. 5. Air mass 48-h back trajectories reaching Tetouan in the period May 2011–April 2012. For each of the four clusters, their main characteristics are provided.

Table 1
Averaged meteorological parameters observed in Tetouan related to the 4 clusters.

Cluster	Path	Nb. of days	T (°C)	WS (m/s)	RH (%)	BLH (m)	P (mm)	PRF (%)
CL1	Local	79 [22%]	18.5 [26.1]	3.1	73.1	396.5	0.7	16.5
CL2	Ocean Slow	118 [32%]	20.4 [31.4]	4.7	57.4	426.7	0.9	13.6
CL3	Mediterranean	144 [39%]	18.7 [26.7]	4.4	73.9	483.4	0.5	11.1
CL4	Ocean Fast	25 [7%]	18.8 [29.4]	6.8	55.4	714.0	5.3	44.0

T (°C) = Temperature [maximum value].
WS (m/s) = Wind speed.
RH (%) = Relative humidity.
BLH (m) = Boundary layer height in Tetouan.
P (mm) = Precipitation.
PRF (%) = Percentage of the days with rainfall.

Table 2
Fine and coarse aerosol mass and chemical composition in Tetouan related to the 4 clusters.

	CL1: Local		CL2: Ocean Slow		CL3: Mediterranean		CL4: Ocean Fast	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Mass	*17.70 ± 0.67*	*12.20 ± 0.24*	*17.40 ± 0.66*	*13.00 ± 0.26*	*18.60 ± 0.71*	*12.50 ± 0.25*	*13.70 ± 0.52*	*11.80 ± 0.24*
EC	3.11 ± 0.14	0.02 ± 0.00	3.22 ± 0.14	0.11 ± 0.00	3.12 ± 0.14	0.21 ± 0.01	3.01 ± 0.13	0.06 ± 0.00
OC	6.01 ± 0.46	0.09 ± 0.01	5.60 ± 0.43	0.09 ± 0.01	5.59 ± 0.42	0.26 ± 0.02	5.20 ± 0.40	0.67 ± 0.05
POM	8.65 ± 2.60	0.13 ± 0.04	8.06 ± 2.42	0.13 ± 0.04	9.39 ± 2.82	0.44 ± 0.13	7.49 ± 2.25	0.96 ± 0.29
Ions	6.15 ± 0.06	4.15 ± 0.04	6.29 ± 0.06	4.05 ± 0.04	6.81 ± 0.07	4.24 ± 0.04	4.62 ± 0.05	4.33 ± 0.04
Dust	1.09	8.88	0.84	8.57	0.16	9.45	0.54	6.63
OC-to-POM	1.2	1.2	1.2	1.2	1.4	1.4	1.2	1.2
Ca^{2+}-to-Dust	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
nss-Sulfate	2.59	0.49	2.76	0.48	2.96	0.41	1.88	0.70
Nitrate	0.99	1.39	0.99	1.39	1.13	1.45	0.69	1.27
Ammonium	0.99	0.24	1.02	0.27	1.13	0.31	0.69	0.10
nss-Potassium	0.40	0.04	0.37	0.02	0.43	0.02	0.28	0.14
Sodium	0.49	0.91	0.51	0.89	0.51	0.99	0.39	0.90
Chloride	0.39	1.10	0.33	1.07	0.42	1.09	0.25	1.17
Oxalate	0.07	0.06	0.07	0.07	0.08	0.06	0.06	0.05
nss-Calcium	0.13	1.07	0.10	1.03	0.02	1.13	0.06	0.80
Sea-salt	1.12	2.46	1.10	2.40	1.19	2.56	0.75	2.34
S/EC	0.83	–	0.86	–	0.95	–	0.62	–
K/EC	0.13	–	0.12	–	0.14	–	0.09	–
OC/EC	1.93	–	1.74	–	1.79	–	1.73	–

Units where applicable: $\mu g/m^3$.
nss-: non-sea-salt.
The italics are the average mass concentration of fine and coarse fractions +/- standard deviation.

12 months of experiment, CL3 fine mass concentrations are driven by high levels of soluble inorganic ions and consequently exceed the fine mass concentrations of the other three clusters by 0.9–4.9 ± 0.64. In the coarse fraction, aerosol masses of CL1 to CL3 are comparable, CL4 values being slightly lower. Inorganic secondary aerosols are found at the highest levels in the fine aerosol mass of CL3. In particular, the high S/EC ratio might indicate inputs from sulfur-rich sources, especially from ship emissions as pointed out by other authors (Marmer and Langmann, 2005; Schembari et al., 2012). The map of maritime traffic density (Fig. 6) suggests intense emissions of fossil fuel combustion aerosols from the Gibraltar Straight and the maritime routes in the area. This source also appears to affect CL1 and CL2, but also CL4, and calls for further sulfur control policies on commercial vessel emissions.

Table 3 presents the mean aerosol concentrations for mass (PM_{10}, $PM_{2.5}$), SO_4^{2-} and NO_3^- obtained from the literature for different Mediterranean sites. Our results regarding the fine aerosol mass are in agreement with those obtained for Porto, Barcelona or Florence. Tetouan sulfate fingerprint (fine fraction) is evidenced, as SO_4^{2-} concentrations are found higher than in the other urban sites.

Fine aerosols are found neutral (Fig. 7). But in the coarse mode, interestingly, more than two thirds of Ca^{2+} (in addition with the other cations) are not balanced by anions. An anion deficit could be explained by the occurrence of carbonate minerals associated with Ca^{2+} at such a coastal city of the Mediterranean. The amount of carbonate was not determined and thus not accounted in the ion balance.

4. Conclusions

Air mass back trajectories arriving at Tetouan have been classified into groups or clusters in an attempt to characterize the main aerosol transport pathways affecting air quality in Northern Morocco. Overall, northerly and westerly winds generally accounted for 2/3 of the year, local recirculation for 1/3. The back trajectory analysis in the one-year period of study, from May 2011 to April 2012, led to four clusters for which meteorological and chemical characteristics have been investigated. The most frequent cluster (CL3: 39%) corresponds to air masses coming from the Mediterranean Basin, including the populated coasts of Spain and of Northern Africa. A key characteristic is the contribution of primary emissions of sulfate (high S/EC values) probably emitted by the intense maritime traffic. A second cluster was found of local origin (CL1: 22%), with a marked contribution from urban aerosols (Rabat, Casablanca) and from biomass burning aerosols.

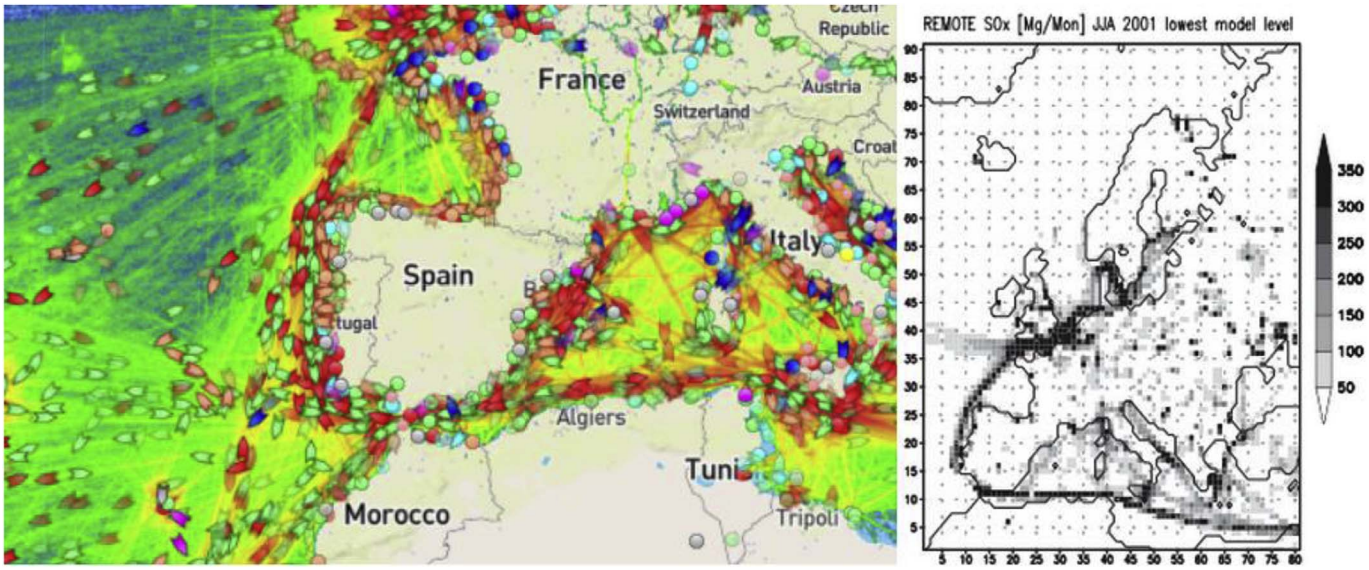

Fig. 6. [Left] Traffic density (all types of vessels) for the year 2015 (Source: www.marinetraffic.com); [Right] EMEP SOx emission inventory JJA 2001 (Vestreng, 2003).

Table 3
Comparison of PM, SO_4^{2-} and NO_3^- concentrations with other locations.

Location	Environment	Study period	Mean concentration (μg/m3)				Reference
			Total	Fine	SO_4^{2-}	NO_3^-	
Tetouan, Morocco	Urban	May. 2011–Apr. 2012	31	18	2.97	1.08	Present study
Crete Island, Greece	Marine boundary layer	Sept. 2001–Apr. 2004	–	8	3.37[a]	0.05	Sciare et al., 2008
Montseny, Spain	Background	Mar. 2002–Dec. 2007		17	3.0	1.7–1.9	Querol et al., 2009a
Bellver, Spain	Suburban	Jul. 2001–Dec. 2007	24	–	–	–	Querol et al., 2009b
Lampedusa, Italy	Background site	2007–2008	32	–	3.65	2.12	Calzolai et al., 2015
Finokalia, Greece	Marine boundary layer	July 2004–July 2006	36	12	4.39	0.10	Koulouri et al., 2008
Barcelona, Spain	Urban background	Jan. 2013–Feb. 2014	23	15	1.68	0.92	Amato et al., 2016
Porto, Portugal	Urban traffic	Jan. 2013–Feb. 2014	35	27	2.0	1.19	Amato et al., 2016
Florence, Italy	Urban background	Jan. 2013–Feb. 2014	19	13	1.54	0.63	Amato et al., 2016
Athens, Greece	Suburban background	Jan. 2013–Feb. 2014	20	11	2.89	0.17	Amato et al., 2016

SO_4^{2-} and NO_3^- concentrations were measured in the aerosol fine fraction.
[a] Is the nss-SO_4. For this study nss-SO_4 = 3.29 μg/m^3. This value was calculated by the following formula: nss-SO_4 = SO_4 − 0.252*Na (Sciare et al., 2003).

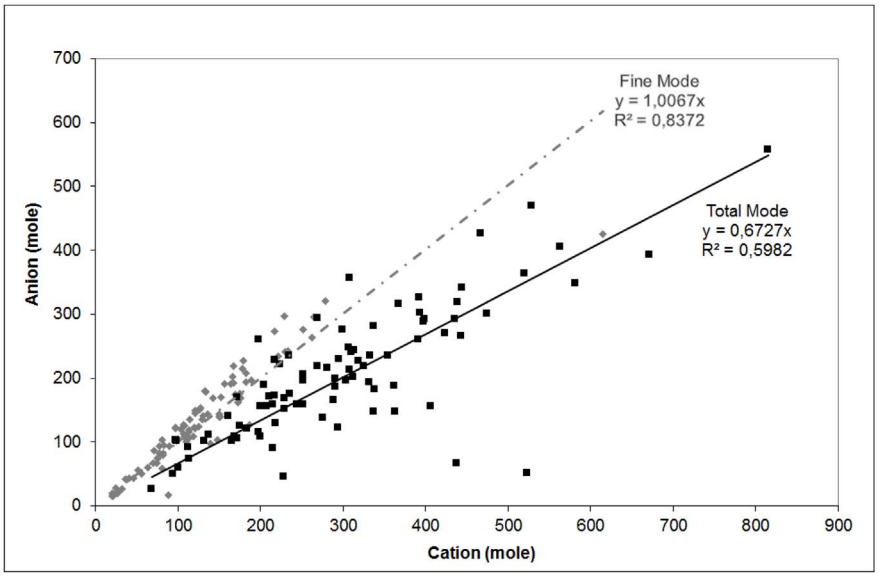

Fig. 7. Ion balance of anionic (Cl^-, NO_3^- and SO_4^{2-}) and cationic (NH_4^+. Na^+, K^+, Ca^{2+}, Mg^{2+}) species in PM_{10} and $PM_{2.5}$ samples from Tetouan city.

Another one (CL2: 32%) defined air masses from the near Atlantic Ocean, affected by pollutants emitted from the Iberian coast. And a last cluster (CL4: 7%) was characterized by rather clean, fast and rainy oceanic air masses, influenced during their last 24 h before reaching Tetouan by similar sources with CL2, but to a lesser extent.

This work underlines the predominant influence of the aerosols emitted in the Western Mediterranean Basin onto Tetouan air quality, and more specifically the influence of the maritime traffic emissions marked by large inputs of primary sulfate. Consequently, the issues related to the oxidative potential of the aerosol phase, like public health, agricultural yields, or cultural heritage, should be of high priority in the national and international research and control strategy plans.

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